Dissolution Behaviour of Fe-Co Alloy in Leaching of Sea-Nodule

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ABSTRACT: Recovery of cobalt from the ammoniacal leaching of polymetallic sea-nodules was often found around 50%, whereas copper and nickel recovered in the range of 90-95%. It is believed that Fe-Co alloy system form during reduction roasting is very stable to ammonia solution. To enhance the cobalt recovery some additives were selected and it was observed that by the use of these additives electrochemical dissolution rate increases in comparison to the system without any additive. Also, the presence of additive lowers the dissolution potential to –454 mV which is a requirement for better recovery of cobalt. Work was further extended with the use of metals powder in pure as well as mixed condition in presence these additives and it was found that cobalt recovery increased above 80%.

1. INTRODUCTION

Polymetallic sea-nodules, available in plenty in the ocean beds particularly in Pacific, Atlantic and Indian oceans, contain strategically important metals like copper, nickel and cobalt in a matrix of oxi-hydroxide minerals of iron and manganese. The concentrations of these elements are comparable to some of the land-based resources. With fast depletion of the resources for copper, nickel and cobalt, recovery of these metals from their lean ores has become inevitable. Under such circumstances worldwide studies are being done for the processing of sea nodules to extract metal values from the ocean nodules. An important commercial method for treating low-grade ores is reduction-roast ammoniacal leaching process (Evans et al., 1979; Caron, 1950; Hewedi and Engle, 1973; Han et al., 1974 and Kukura et al., 1979). Cobalt extraction, however, is often found to be low (~50%) with this process (Siemens et al., 1977; Lee et al., 1985 and Jana et al., 1999). This may be attributed, in part, to: (i) Co-precipitation of cobalt with iron and manganese and its adsorption on the finely divided oxi-hydroxide residues, (ii) Electrochemical interaction between cobalt and other metals present in the roasted sea nodules during ammoniacal leaching (Kasherininov, 1960; Vu and Han, 1977 and Osseo-Asare et al., 1983) and (iii) Fe-Co alloy formation during roasting, which is difficult to leach due to passive film formation.

The work reported here, is on the polarization behaviour of iron-cobalt alloy in NH_3-H_2O-CO_3 system in presence of some additives to see their effect on dissolution of the alloy system. Since the dissolution of metallic phases is an electrochemical process, polarization technique may provide valuable and quick information to understand the dissolution mechanism of the metals. Also, experiments have been carried out to study the dissolution of metals powder alone and in mixed condition in presence of the additives.

2. EXPERIMENTAL

Fe-Co alloy was prepared from iron and cobalt powders. Amount of iron and cobalt were taken corresponding to the composition of sea-nodules. After mixing and compaction, the pellets were melted in cylindrical crucible of 3.5 cm diameter in inert atmosphere. To prepare specimens for polarization studies, Fe-Co alloy sample was cut into discs having 3 mm thickness. Samples were polished and prepared for electrochemical studies. All the solutions of weak and strong electrolytes were prepared using 100 gpl ammonia solution. Saturated calomel electrode

was used as reference electrode and potentiostat/ galvanostat AutoLab-12 was used for electrochemical studies. Appropriate amount of metals, present in sea nodules, in the form of metal powder was taken in NH_3-H_2O-CO_3 system to determine their dissolution behaviour in pure and mixed condition in presence of additive.

3 RESULTS AND DISCUSSION

It has been reported that during reduction roasting Fe-Co alloys are formed which may not react with ammoniacal solution easily. To study the dissolution of Fe-Co electrode in ammoniacal solution, some electrochemical polarization studies were performed on as received as well as on the electrochemically pretreated electrode material at –1V for 5 minutes (figure 1).

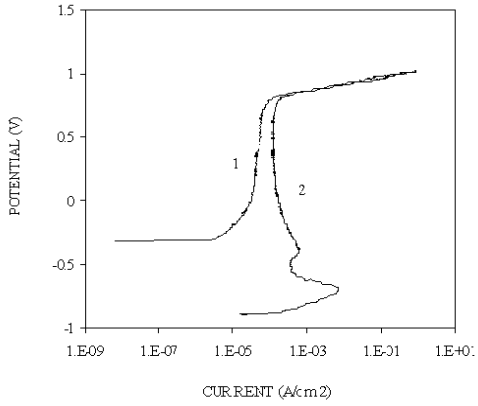

Fig. 1: Potentiodynamic polarization of Fe-Co alloy in 100 gpl ammonia and 60 gpl CO_2 solution; 1—untreated electrode and 2—treated electrode at –1V for 5 minutes

Such treatment is generally done to remove any oxide or hydroxide present on the metal surface. Potentiodynamic polarization curves shown in figure reveal that dissolution current in case of untreated alloy sample (Curve 1) is low to that of treated one. This nature of curve is indicative of some protective film on the untreated electrode surface. In Table 1, a summarized results are given for electrochemical parameters: dissolution rate and dissolution potential in presence of various additives. It was observed that dissolution rate as well as dissolution potential were higher in presence of NaCl and Na_2SO_4 in ammoniacal solution. Figure 2 shows polarization plot for the Fe-Co alloy system in the presence and absence of Na_2SO_4, where it is observed that open circuit potential shifted to more negative potential (-454 mV) and anodic current (2.82 $\mu A/cm^2$) found to be high in the presence of additive.

Table 1: The electrochemical parameters (dissolution rate and dissolution potential)

Electrolyte	*Dissolution rate, $\mu A/cm^2$*	$E_{dissolution\ (obs)}$, *V*	$E_{dissolution\ (cal)}$, *V*
100 gpl NH_3 solution	2.38	-0.299	-0.297
5% $(NH_4)_2SO_4$	2.30	-0.308	-0.308
5% NaCl	2.53	-0.341	-0.337
5% Na_2SO_4	2.82	-0.454	-0.456

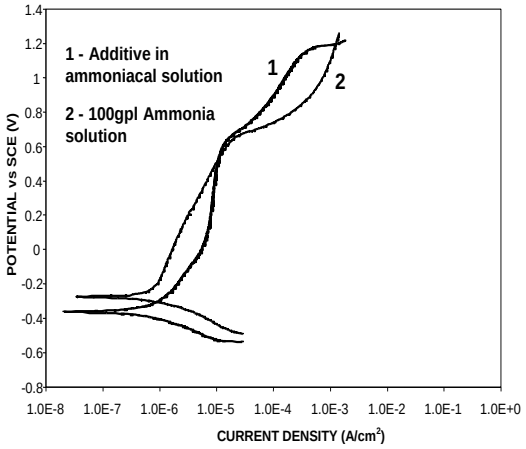

Fig. 2: Potentiodynamic polarization of Fe-Co alloy in 100 gpl ammonia and 60 gpl CO_2 solution; 1—with additive and 2—without additive

This behaviour indicates removal of any film from the surface and more dissolution rate respectively. Table 2 presents the recovery of metals from pure metal powders during ammoniacal leaching.

Table 2: Leaching of individual metal powder

Leachant concentration	*Metal*	*% Recovery*

Ammonia-100 gpl + Co_2–60 gpl	Cu	87.9
	Fe	0.1
	Zn	94.2
	Co	86.7
	Ni	93.8
	Mn	3.4

From the Table 2 we see that the recovery of copper, nickel and cobalt was above 85% when there was no interference of other metals. But when the mixed metal systems were selected for the same study (Table 3), it was observed that recovery of cobalt drastically reduced to 58% in presence of iron and it further reduced to 17.42% in presence of manganese.

Table 3: Effect of various metals on cobalt recovery

Metal	% Recovery			
	Cu	Fe	Zn	Co
Co	-	-	-	86.9
Cu + Co	86.8	-	-	96.4
Fe + Co	-	0.06	-	58.6
Zn + Co	-	-	94.1	96.1
Mn + Co	-	-	-	17.42

This observation indicates that the in the presence of iron and manganese in the system reduces the recovery of cobalt. Effect of additive on cobalt recovery, in presence of iron, is given in Table 4.

Table 4: Effect of additive on the cobalt recovery

Metal powder leached in ammo. solution	*Additive*	*% Fe level in leach solution in 48 hrs*	*% Co Recovery*
Co	-	-	86.9
Co + Fe	-	-	58.6
Co + Fe	Sodium sulphate	-	90.0
Fe	-	0.00637	-
Fe	Sodium sulphate	0.00065	-

Here, it was observed that in the presence of additive cobalt recovery increased from 58.6% (in absence of additive) to 90.0%. Reason behind this may due to reduced level of Iron in the solution in presence of additive, which is also shown in the same Table. Also, precipitate of iron obtained in presence of additive more and fast; it was characterized as goethite using X-ray difftraction method.

4. CONCLUSIONS

1. Recovery of Co drastically comes down when Fe + Co powders were leached together. Same was true with Mn Powder also.
2. Additive improved the recovery of cobalt. Possible reason is that on addition of Na_2SO_4, precipitation of iron as goethite, was very fast & thus Co ion adsorption reduced.
3. Electrochemical studies revealed that Fe-Co alloy surface is covered with a protective coating, which does not allow alloy to go in the solution.
4. Additive brings down the electrode potential to cathodic direction and therefore, increased dissolution rate was observed.
5. Based on the above studies experiments were conducted with Na_2SO_4 addition in actual leaching of reduction-roast polymetallic sea-nodules. Cobalt recovery in this was improved to 80%.

REFERENCES

[1] Caron, M.H., Trans. AIME, 188, 67-90, (1950).
[2] Evans, D.J.I., Shoemaker, R.S. and Veltman, H., eds. Proceed. Intl. Laterite Symposium, AIME, New York, NY, 1979.
[3] Han, K.N., Hoover, M. and Fuerstenau, D.W., Intl. Jour. Min. Process, 1, 215-30 (1974).
[4] Hewedi, M.A. and Engle, L.R., Intl. Symposium on Hydrometallurgy, D.J.I. Evans and R.S. Shoemaker, eds., AIME, New York, NY, pp. 806-58, (1973).
[5] Jana, R.K. and Pandey, B.D., Premchand, Hydrometallurgy, 53, 45-66 (1999).
[6] Kasherininov, G.O., J. Applied Chem., USSR, 33, 1225-30 (1960).
[7] Kukura, M.E., Stevens, L.G. and Auck, Y.T., Proceed. Intl. Laterite Symposium, D.J.I. Evans, R.S. Shoemaker, and H. Veltman, eds., AIME, New York, NY, pp. 527-52 (1979).
[8] Lee, J.W., Osseo-Asare, K. and Pickering, H.W., J. Electrochem. Soc., 132, 550-555 (1985).

[9] Osseo-Asare, K., Lee, J.W., Kim, H.S. and Pickering, H.W, Metallurgical Trans. B, 14B, 571-76 (1983).

[10] Siemens, R.E. and Corrick, Min. Cong. J., 63(1), 29-34 (1977).

[11] Vu, C. and Han, K.N., Trans. IMM, Section C, 86, 119-25 (1977).